Electrochemical Promotion of Catalysts for the Gas Phase Oxidation of Hydrocarbons

J. Eaves , G. Fóti, Ch. Comninellis,

EPFL- Institute of Chemical Engineering, Swiss Federal Institute of Technology, CH-1015 Lausanne.

It has been found that when a current or a potential is applied to the solid electrolyte cells of the type

reactants(g), catalyst | solid electrolyte | counter electrode, O_2(g)

the catalytic activity and selectivity of the catalyst film can be dramatically altered. The increase in catalytic rate can be to a factor 100 or more higher than the open circuit reaction rate, and it can be up to a factor of 10^5 higher than the rate of the electrochemical reaction induced simultaneously on the catalyst. This effect, called Electrochemical Promotion (EP), is believed to be due to an electrochemically controlled fast migration of promoting (*spillover*) ions from the solid electrolyte onto the gas exposed catalyst surface. The presence of these species is supposed to modify the binding strength of chemisorbed reactants and intermediates [1-6].

The aim of this work was to contribute in a further elucidation of the origin of the EP effect. In certain cases, the response of the catalytic system to the potential step applied can be divided in two parts [7]. One of them is an enhancement of the catalyst activity to a steady state reaction rate *r* much higher than the initial reaction rate r_o. A much slower further increase of reaction rate may also be observed resulted in a reaction rate *r'*. The first step was attributed to spillover of promoting species whereas the second step was explained by chemical modification of the catalyst surface. In this work, the first step of enhancement was studied by *in situ* cyclic voltammetry.

The EP effect was applied for ethylene and propylene combustion on IrO_2 and Rh catalysts. The solid electrolyte was yttria stabilized zirconia (YSZ). Changes, induced on the catalyst surfaces under EP conditions were investigated by means of high temperature *in situ* cyclic voltammetry. The voltammetric scan was applied in a small potential window around the open circuit potential, in order to induce reversible polarisation changes at the electrochemically active part of the catalyst surface. For the Rh catalyst, unlike in the previous studies of this type [7,8], a two compartment reactor was used.

Two main informations were drawn from the voltammogram shape : the voltammetric charge induced during the potential scan and the polarisation resistance of the system (fig.1). The influence of the gas composition and of the catalyst loading on these two parameters were investigated.

The voltammetric charge is strongly dependent on the scan rate ν (fig.2) allowing to divide it to an inner and an outer charge by adapting Trasatti's method for solid electrochemistry [7,8]. A proportionality between the inner voltammetric charge and the thickness of the catalyst film can be observed. As the inner voltammetric charge is associated with a gas exposed catalyst surface, these results suggest that, under EP conditions, the whole surface of the catalyst can be modified.

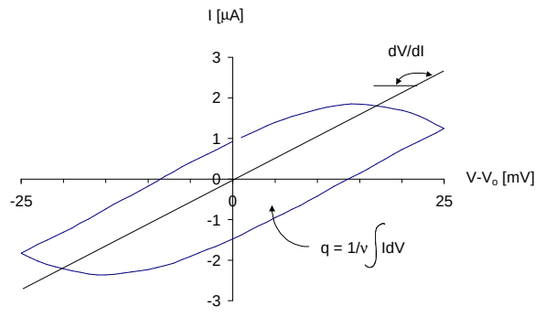

Fig.1: A typical cyclic voltammogram of a Rh/YSZ catalyst. Rh loading: 2.4g/m^2, T=350°C, P_{O2}=20kPa, ν = 40mV/s.

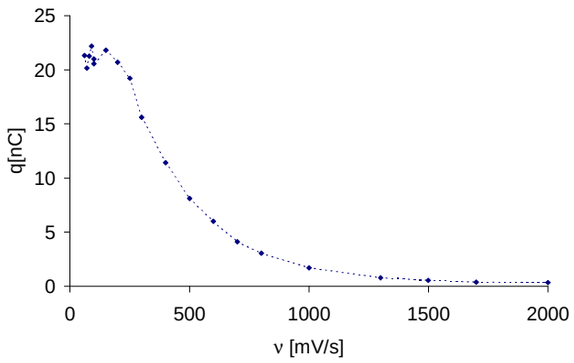

Fig.2: Voltammetric charge as a function of scan rate. Rh/YSZ catalyst, Rh loading : 0.4g/m^2, T=350°C, P_{O2}=20kPa

References:

[1] C.G.Vayenas, S.Bebelis and S. Neophytides, J.Phys. Chem.,92 (1988) 5083
[2] C.G.Vayenas, S.Bebelis I.V Yetekakis and H.G.Lintz, Catalysis Today, 11 (1992) 303
[3] C.G.Vayenas, S.Bebelis, S. Neophytides and I.V.Yetekakis, Nature, 343 (1990) 625
[4] E.Varkaraki, J. Nicole, E.Plattner, Ch.Comninellis and C.G.Vayenas, J. Appl. Electrochem., 25 (1995) 978
[5] J.Pritchard, Nature, 343 (1990) 592
[6] C.G.Vayenas, M.M.Jaksic, S.Bebelis and S. Neophytides, Modern aspects of Electrochemistry, JO'M.Bokris,Editor,Vol.29 (1996) 57
[7] J. Nicole, Ch.Comninellis, Solid State Ionics, 136-137 (2000) 687-692
[8] S.Wodiunig, V.Patsis, Ch.Comninellis 136-137 (2000) 813-817